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(54) Title: CATALYST SYSTEM AND OLEFIN POLYMERISATION PROCESS

(57) Abstract: Methods of making supported chromium catalyst system and processes of polymerizing ethylene using the supported chromium catalyst system are disclosed. A method of forming a catalyst system in a polymerization reactor includes contacting a supported chromium catalyst and a metal alkyl cocatalyst by cofeeding the catalyst and cocatalyst to the reactor or feeding the catalyst and cocatalyst separately to the reactor, to form a catalyst system. The catalyst and cocatalyst are not pre-contacted prior to the feeding or cofeeding step. The catalyst system can be contacted with ethylene and optional alpha-olefin comonomer to form polyethylene.

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**CATALYST SYSTEM AND OLEFIN POLYMERISATION PROCESS**CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 60/387,006, filed June 6, 2002, the disclosure of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The invention is generally directed to methods making supported chromium catalyst systems and methods of polymerizing ethylene using such catalyst systems. In particular, the invention provides methods of forming a supported chromium catalyst-metal alkyl cocatalyst system in a polymerization reactor, and methods of polymerizing ethylene with or without addition of comonomer using the catalyst system.

BACKGROUND

[0003] Chromium catalysts, sometimes termed Phillips catalysts, are well known catalysts for olefin polymerization. In these catalysts, a chromium compound, such as chromium oxide, is supported on a support of one or more inorganic oxides such as silica, alumina, zirconia or thoria, and activated by heating in a non-reducing atmosphere. U.S. Patent No. 2,825,721 describes chromium catalysts and methods of making the catalysts. It is also known to increase polymer melt index by using a silica-titania support as disclosed, for example, in U.S. Patent No. 3,887,494.

[0004] European patent application EP 1 172 381 A1 discloses a method for producing ethylene polymers reputedly having improved environmental stress crack resistance (ESCR) using a trialkylaluminum compound-carried chromium catalyst. The activated chromium compound on an inorganic support is treated with a trialkylaluminum compound in an inert hydrocarbon solvent and the solvent removed to form a trialkylaluminum-carried chromium catalyst. EP 1 172 381 A1 discloses that the time of contact with the solvent must be minimized to avoid over-reduction and associated degradation of polymer properties. The

reference further teaches that for ESCR and impact resistance it is essential to use hydrogen in a carefully controlled hydrogen-ethylene ratio. The need for careful control of contact time, hydrogen concentration, and amount of trialkylaluminum used in the catalyst synthesis in order to achieve desired polymer properties limits the usefulness of such methods.

[0005] U.S. Patent No. 6,174,981 discloses a process of polymerizing ethylene and at least one C<sub>3</sub> to C<sub>8</sub> mono-olefin in the presence of a catalyst including chromium supported on a silica-titania support and a trialkylboron compound. The process, however, produces resins that generally have density and HLMI (high load melt index, I<sub>21.6</sub>) values lower than would be desirable for environmentally demanding applications such as for pipe or drum resins.

[0006] Other relevant references include EP 0279890; WO 01 32307; DE 2622755; and US 4,877,763.

## SUMMARY OF THE INVENTION

[0007] In one embodiment, the invention provides a method of forming a catalyst system in a polymerization reactor, by providing a supported chromium catalyst and a trialkylaluminum cocatalyst; and contacting the catalyst and cocatalyst to form a catalyst system. The catalyst and cocatalyst are contacted by cofeeding the catalyst and cocatalyst to the reactor, or feeding the catalyst and cocatalyst separately to the reactor. The catalyst and cocatalyst are not contacted prior to the step of feeding or cofeeding.

[0008] In another embodiment, the invention provides a method of forming a catalyst system in a polymerization reactor, by providing a supported chromium catalyst activated at a temperature of greater than 600 °C and a Group 13 metal alkyl cocatalyst; and contacting the catalyst and cocatalyst to form a catalyst system. The catalyst and cocatalyst are contacted by cofeeding the catalyst and cocatalyst to the reactor, or feeding the catalyst and cocatalyst separately to the reactor. The catalyst and cocatalyst are not contacted prior to the step of feeding or cofeeding.

[0009] In another embodiment, the invention provides catalyst systems produced by the inventive processes, polyethylene resins produced using these catalyst

systems, and articles formed of or including the polyethylene resins. Typical articles include, for example, pipes and drums.

[0010] In another embodiment, the invention provides a process of polymerizing ethylene in a reactor, by providing a supported chromium catalyst; providing a cocatalyst selected from metal alkyls of group 13 metals, and mixtures thereof; contacting the catalyst and cocatalyst by cofeeding the catalyst and cocatalyst to the reactor or feeding the catalyst and cocatalyst separately to the reactor, to form a catalyst system; and contacting the catalyst system, under polymerization conditions, with ethylene to form polyethylene. The catalyst and cocatalyst are not contacted prior to the step of feeding or cofeeding, and the process is carried out without addition of alpha-olefin comonomer.

[0011] In another embodiment, the invention provides a process of polymerizing ethylene in a reactor, by providing a supported chromium catalyst activated at a temperature of greater than 600 °C; providing a cocatalyst selected from metal alkyls of group 13 metals, and mixtures thereof; contacting the catalyst and cocatalyst by cofeeding the catalyst and cocatalyst to the reactor or feeding the catalyst and cocatalyst separately to the reactor, to form a catalyst system; and contacting the catalyst system, under polymerization conditions, with ethylene and alpha-olefin comonomer to form polyethylene. The catalyst and cocatalyst are not contacted prior to the step of feeding or cofeeding.

[0012] In another embodiment, the invention provides a process of polymerizing ethylene in a reactor, by providing a supported chromium catalyst; providing a cocatalyst selected from metal alkyls of group 13 metals, and mixtures thereof; contacting the catalyst and cocatalyst by cofeeding the catalyst and cocatalyst to the reactor or feeding the catalyst and cocatalyst separately to the reactor, to form a catalyst system; and contacting the catalyst system, under polymerization conditions, with ethylene and alpha-olefin comonomer to form polyethylene. The catalyst and cocatalyst are not contacted prior to the step of feeding or cofeeding, and the polymerization is carried out at a temperature greater than 100 °C.

[0013] In another embodiment, the invention provides a process of polymerizing ethylene in a reactor, by providing a supported chromium catalyst; providing a trialkylaluminum cocatalyst; contacting the catalyst and cocatalyst by cofeeding

the catalyst and cocatalyst to the reactor or feeding the catalyst and cocatalyst separately to the reactor, to form a catalyst system; and contacting the catalyst system, under polymerization conditions, with ethylene and alpha-olefin comonomer to form polyethylene. The catalyst and cocatalyst are not contacted  
5 prior to the step of feeding or cofeeding.

[0014] In other embodiments, the invention provides polyethylene resins produced by the inventive processes, and articles formed from or including the polyethylene resins. Typical articles include, for example, containers for household industrial chemicals, drainage, pressure and conduit pipe, industrial  
10 bulk containers such as drums (typically 30 or 50 gallon drums), and geomembranes.

#### DETAILED DESCRIPTION

##### Catalyst System

[0015] The catalyst system includes a supported chromium catalyst and a  
15 cocatalyst. Supported chromium catalysts are well known, and are described, for example, in U.S. Patent No. 2,825,721. In general, such catalysts include a chromium compound supported on an inorganic oxide matrix. Typical supports include silicon, aluminum, zirconium and thorium oxides, as well as combinations  
20 thereof. Various grades of silica and alumina support materials are widely available from numerous commercial sources.

[0016] In a particular embodiment, the support is silica. A suitable silica is a high surface area, amorphous silica, such as a material marketed under the tradenames of Davison 952 or Davison 955 by the Davison Chemical Division of W.R. Grace  
25 and Company. These silicas are in the form of spherical particles obtained by a spray-drying process, and have a surface area of about 300 m<sup>2</sup>/g, and a pore volume of about 1.65 cm<sup>3</sup>/g. Granular silica can also be used.

[0017] In another embodiment, the support is a silica-titania support. Silica-titania supports are well known in the art and are described, for example, in U.S.  
30 Patent No. 3,887,494. Silica-titania supports can be produced as described in U.S. Patent Nos. 3,887,494, 5,096,868 or 6,174,981 by "cogelling" or coprecipitating silica and a titanium compound. Such a cogel can be produced by contacting an

alkali metal silicate such as sodium silicate with an acid such as sulfuric acid, hydrochloric acid or acetic acid, or an acidic salt. The titanium component can be conveniently dissolved in the acid or alkali metal silicate solution and co-precipitated with the silica. The titanium compound can be incorporated in the acid in any form in which it subsequently will be incorporated in the silica gel formed on combination of the silicate and the acid and from which form it is subsequently convertible to titanium oxide on calcination. Suitable titanium compounds include, but are not limited to, halides such as  $\text{TiCl}_3$  and  $\text{TiCl}_4$ , nitrates, sulfates, oxalates and alkyl titanates. In instances where carbon dioxide is used as the acid, the titanium can be incorporated into the alkali metal silicate itself. When using acidic salts, the titanium compound can be incorporated in the alkali metal silicate and in such instances, convenient titanium compounds are water soluble materials which do not precipitate the silicate, *i.e.*, are those convertible to titanium oxide on calcination such as, for example, various titanium oxalates, such as  $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$  and  $\text{Ti}_2(\text{C}_2\text{O}_4)_3 \cdot \text{H}_2\text{O}$ . As used herein, the term "silica-titania" support includes supports formed by any of these coprecipitation or cogel processes, or other processes by which titania and silica are both incorporated into the support.

[0018] In another embodiment, titanium is incorporated by surface-modifying a supported chromium catalyst. As used herein, the term "titanium surface-modified supported chromium catalyst" is meant to include any supported chromium catalyst that is further modified to include titanium; see, *e.g.*, C.E. Marsden, *Plastics, Rubber and Composites Processing and Applications*, 21 (1994), 193-200. For example, it is known to modify supported chromium catalysts by slurring the chromium catalyst in a hydrocarbon and contacting the slurry with a titanium alkoxide,  $\text{Ti}(\text{OR})_4$ , and heating to form a dried, titanium surface-modified supported chromium catalyst. The alkyl group R of the alkoxide can be a  $\text{C}_3$  to  $\text{C}_8$  linear or branched alkyl group; a particular example of a suitable titanium alkoxide is titanium tetraisopropoxide. Another method of titanating a supported chromium catalyst is to heat a solid supported chromium catalyst and a solid titanium compound such as titanium tetraacetoacetate under gas fluidization

conditions, whereby the titanium compound sublimes and titanium is deposited on the supported chromium catalyst, possibly as a titanium oxide.

[0019] The titanium compound preferably is generally present in an amount of from a lower limit of 0.5 % or 1 % or 2 % or 3% or 5 % titanium by weight to an upper limit of 12 % or 10 % or 8 % or 6 % by weight, with ranges from any lower limit to any upper limit being contemplated.

[0020] The chromium compound can be incorporated in any convenient method known in the art. For example, a chromium compound and optionally a titanium compound, is dissolved in an acidic material or the silicate and thus coprecipitated with the silica. A suitable chromium compound for this method is chromic sulfate. Another method to incorporate a chromium compound into the catalyst system is to use a hydrocarbon solution of a chromium compound convertible to chromium oxide to impregnate the support after it is spray dried or azeotrope dried (*i.e.*, a xerogel). Exemplary of such materials are t-butyl chromate, chromium acetylacetonate, and the like. Suitable solvents include, but are not limited to, pentane, hexane, benzene, and the like. Alternatively, an aqueous solution of a chromium compound simply can be physically mixed with the support. These types of catalyst systems are disclosed in U.S. Pat. No. 3,887,494.

[0021] Chromium can be present in the catalyst an amount from a lower limit of 0.1 or 0.5 or 0.8 or 1.0 % or 1.5 % by weight to an upper limit of 10 % or 8 % or 5 % or 3 % by weight, with ranges from any lower limit to any upper limit being contemplated.

[0022] Supported chromium catalysts are commercially available. Suitable commercially available chromium catalysts include HA30W and HA30LF, products of W.R. Grace & Co., containing about 1% Cr by weight.

[0023] Supported titanium-chromium catalysts are also commercially available. Suitable commercially available titanium-chromium catalysts include titanium-surface modified chromium catalysts from PQ Corporation such as C-23307, C-25305, C-25345, C-23305, and C-25307. Commercially available titanium-surface modified chromium catalysts typically contain about 1-5 % Ti and 1% Cr by weight.

[0024] In any of the supports described above, the support can also include other inorganic oxides, such as alumina, thoria or zirconia. Further, the support can be treated by various methods known in the art, such as by fluoridation.

[0025] The catalyst is activated prior to use by heating the dry catalyst system in a non-reducing atmosphere, conveniently in air or in an oxygen-enriched atmosphere. The calcination temperature can be from 400 or 450 or 500 or 550 °C to 900 or 800 or 700 °C, with ranges from any lower limit to any upper limit being contemplated. In a particular embodiment, the calcination temperature is greater than 600 °C. Typical heating times can be for 30 minutes to 50 hours, with 2 to 20 hours being generally sufficient. Without wishing to be bound by theory, it is generally believed that the calcination procedure results in at least a substantial portion of the chromium being oxidized to a hexavalent form. Calcination is conveniently carried out in a stream of fluidizing air wherein the stream of fluidizing air is continued as the material is cooled. As a specific example, the catalyst can be placed in a cylindrical tube and fluidized in dry air at about 2 feet per minute linear velocity while being heated to a pre-determined temperature, typically 400 to 900 °C, and held at temperature for about 6 hr. The activated catalyst is recovered as a free-flowing powder. Catalysts can also be activated with a sequence of gaseous compositions. For example, the catalyst can be first heated in nitrogen to a first temperature, followed by air at a second temperature, then cooled under nitrogen to ambient temperature. Activation can also involve a short period using carbon monoxide as the fluidization gas between the air and /or nitrogen steps. At the end of activation the catalyst is cooled to ambient temperature and stored under nitrogen for use in the polymerization reactor.

[0026] The catalyst is used in conjunction with a cocatalyst, as described below. In general, the cocatalyst can be a metal alkyl of a Group 13 metal. The cocatalyst can be a compound of formula  $MR_3$ , where M is a group 13 metal, and each R is independently a linear or branched  $C_1$  or  $C_2$  or  $C_4$  to  $C_{12}$  or  $C_{10}$  or  $C_8$  alkyl group. Mixtures of two or more such metal alkyls are also contemplated, and are included within the term "cocatalyst" as used herein.



[0027] In a particular embodiment, M is boron. In a specific aspect of this embodiment, each R is ethyl; *i.e.*, the cocatalyst is triethylboron (TEB).

[0028] In another particular embodiment, M is aluminum. Particular examples of suitable cocatalysts in this embodiment are tri-isobutylaluminum (TIBAL) and tri-  
5 n-octylaluminum (TNOA).

[0029] In some embodiments, the cocatalyst can be used in an amount in accordance with (I), or (II) or both (I) and (II):

[0030] The concentration of cocatalyst in the reaction diluent is from 0.1 or 1 or 5 or 10 or 20 or 30 or 40 ppm to 100 or 90 or 80 or 70 or 60 ppm, with ranges from  
10 any lower limit to any upper limit being contemplated. The concentration of cocatalyst is expressed as parts by weight of cocatalyst per million parts by weight of the diluent phase.

[0031] The ratio of moles of cocatalyst to moles of chromium is from a lower limit of 0.1:1 or 0.5:1 or 1:1 or 2:1 or 3:1 or 4:1 to an upper limit of 10:1 or 8:1 or  
15 7:1 or 6:1, with ranges from any lower limit to any upper limit being contemplated.

[0032] More or less cocatalyst can be used, depending upon the amount of poisons present in the reaction system. Poisons in the reactor that can consume or deactivate the cocatalyst include, for example, as oxygen, water, carbon monoxide  
20 or carbon dioxide.

[0033] In one embodiment, the catalyst system is formed in a polymerization reactor, by providing a supported chromium catalyst and a trialkylaluminum cocatalyst as described above; and contacting the catalyst and cocatalyst to form a catalyst system. The catalyst and cocatalyst can be contacted by cofeeding the  
25 catalyst and cocatalyst to the reactor, or feeding the catalyst and cocatalyst separately to the reactor. The catalyst and cocatalyst are not contacted prior to the step of feeding or cofeeding.

[0034] In another embodiment, the catalyst system is formed in a polymerization reactor, by providing a supported chromium catalyst activated at a temperature of  
30 greater than 600 °C and a Group 13 metal alkyl cocatalyst as described above; and contacting the catalyst and cocatalyst to form a catalyst system. The catalyst and cocatalyst can be contacted by cofeeding the catalyst and cocatalyst to the reactor,

or feeding the catalyst and cocatalyst separately to the reactor. The catalyst and cocatalyst are not contacted prior to the step of feeding or cofeeding.

#### Polymerization Process

- 5 [0035] The methods of the invention can generally be carried out in a slurry reactor, such as a stirred slurry reactor or a slurry loop reactor, or in a gas phase reactor. For illustrative purposes, the methods are described below with particular reference to a slurry loop reactor. However, it should be appreciated that the methods are not limited to this particular reactor configuration.
- 10 [0036] A slurry loop olefin polymerization reactor can generally be described as a loop-shaped continuous tube. In some instances, the reactor design may be generally "O" shaped. One or more fluid circulating devices, such as an axial pump, urge the reactor constituents within the tube in a desired direction so as to create a circulating current or flow of the reactor constituents within the tube.
- 15 Desirably, the fluid circulating devices are designed to provide high velocity of motion and a very intensive and well-defined mixing pattern of the reactor constituents. The reactor may be totally or partially jacketed with cooling water in order to remove heat generated by polymer polymerization.
- [0037] In the slurry loop olefin polymerization reactor, the polymerization
- 20 medium includes monomer, optional comonomer, and a hydrocarbon solvent or diluent, advantageously aliphatic paraffin such as propane, isobutane, hexane, heptane, or cyclohexane, for example, or an aromatic diluent such as toluene, or mixtures thereof. The polymerization is carried out at a temperature of from a lower limit of 50 or 60 or 70 or 80 or 90 °C to an upper limit of 150 or 140 or 130
- 25 or 120 or 110 or 100 °C, with ranges from any lower limit to any upper limit being contemplated. In a particular embodiment, the polymerization is carried out at a temperature of greater than 95 °C or greater than 100 °C. In another particular embodiment, the polymerization is carried out at a temperature  $T_R$  of from greater than 100 °C to 110 °C (i.e.,  $100\text{ °C} < T_R \leq 110\text{ °C}$ ). Pressures can vary from
- 30 about 100 to about 700 psia (0.69-4.8 MPa). Additional description is given in U.S. Patent Nos. 5,274,056 and 4,182,810 and PCT publication WO 94/21962. As such, the reactor constituents generally are a combination of both solids, such

as supported catalyst and polymerized olefin, and liquids, such as those described above. The percentage of solids within the reactor constituents may be as high as 60 wt % of the reactor constituents. Typically, the weight percent of solids is in the range of 45 to 55 wt %.

5 [0038] The slurry loop olefin polymerization reactor may be operated in a single stage process or in multistage processes. In multistage processing, the polymerization of olefins is carried out in two or more reactors. These reactors can be configured in series, in parallel, or a combination thereof.

[0039] The methods of the invention are used in the slurry polymerization of  
10 ethylene to form polyethylene homopolymer or copolymer having the properties described herein. In some embodiments, the methods are carried out without addition of comonomer; *i.e.*, the monomer feed is essentially ethylene, with no comonomer intentionally added, although it should be appreciated that minor amounts of other polymerizable olefins may be present in the ethylene feedstock,  
15 typically less than 1% or less than 0.5% or less than 0.1% or less than 0.05% or less than 0.01% by weight. Without wishing to be bound by theory, it is believed that processes of the invention result in formation in situ of polymerizable comonomer, which is then incorporated into the polyethylene. Thus, polyethylenes formed in processes of the invention even without addition of  
20 comonomer can have short chain branching and other properties typically associated with polyethylene copolymers.

[0040] In some embodiments, both ethylene and at least one comonomer are provided to the reactor. Suitable comonomers include  $\alpha$ -olefins, such as  $C_3$ - $C_{20}$   $\alpha$ -olefins or  $C_3$ - $C_{12}$   $\alpha$ -olefins. The  $\alpha$ -olefin comonomer can be linear or branched,  
25 and two or more comonomers can be used, if desired. Examples of suitable comonomers include linear  $C_3$ - $C_{12}$   $\alpha$ -olefins, and  $\alpha$ -olefins having one or more  $C_1$ - $C_3$  alkyl branches, or an aryl group. Specific examples include propylene; 3-methyl-1-butene; 3,3-dimethyl-1-butene; 1-pentene; 1-pentene with one or more methyl, ethyl or propyl substituents; 1-hexene with one or more methyl, ethyl or  
30 propyl substituents; 1-heptene with one or more methyl, ethyl or propyl substituents; 1-octene with one or more methyl, ethyl or propyl substituents; 1-nonene with one or more methyl, ethyl or propyl substituents; ethyl, methyl or

dimethyl-substituted 1-decene; 1-dodecene; and styrene. It should be appreciated that the list of comonomers above is merely exemplary, and is not intended to be limiting. Preferred comonomers include propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene and styrene.

- 5 [0041] Other useful comonomers include conjugated and non-conjugated dienes, which can be included in minor amounts in terpolymer compositions. Non-conjugated dienes useful as co-monomers preferably are straight chain, hydrocarbon diolefins or cycloalkenyl-substituted alkenes, having 6 to 15 carbon atoms. Suitable non-conjugated dienes include, for example: (a) straight chain
- 10 acyclic dienes, such as 1,4-hexadiene and 1,6-octadiene; (b) branched chain acyclic dienes, such as 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; and 3,7-dimethyl-1,7-octadiene; (c) single ring alicyclic dienes, such as 1,4-cyclohexadiene; 1,5-cyclo-octadiene and 1,7-cyclododecadiene; (d) multi-ring alicyclic fused and bridged ring dienes, such as tetrahydroindene; norbornadiene;
- 15 methyl-tetrahydroindene; dicyclopentadiene (DCPD); bicyclo-(2.2.1)-hepta-2,5-diene; alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes, such as 5-methylene-2-norbornene (MNB), 5-propenyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, and 5-vinyl-2-norbornene (VNB); and (e) cycloalkenyl-substituted alkenes, such
- 20 as vinyl cyclohexene, allyl cyclohexene, vinyl cyclooctene, 4-vinyl cyclohexene, allyl cyclodecene, and vinyl cyclododecene. Of the non-conjugated dienes typically used, the preferred dienes are dicyclopentadiene, 1,4-hexadiene, 5-methylene-2-norbornene, 5-ethylidene-2-norbornene, and tetracyclo-( $\Delta$ -11,12)-5,8-dodecene. Particularly preferred diolefins are 5-ethylidene-2-norbornene
- 25 (ENB), 1,4-hexadiene, dicyclopentadiene (DCPD), norbornadiene, and 5-vinyl-2-norbornene (VNB).

[0042] The amount of comonomer used will depend upon the desired density of the polyolefin and the specific comonomers selected. One skilled in the art can readily determine the appropriate comonomer content appropriate to produce a

30 polyolefin having a desired density. As used herein, the term "comonomer" includes mixtures of two or more comonomers.

[0043] The catalyst and cocatalyst can be fed separately into the slurry reactor, such as through separate inlets or sequentially through a common inlet, or can be co-fed. As used herein, the term "co-fed" means that catalyst and cocatalyst feedstreams are combined and fed together into the reactor. This cofeeding or combining of feedstreams, is different from the pre-contacting required in the prior art, such as in EP 1 172 381, wherein a supported chromium catalyst is treated with trialkylaluminum cocatalyst and dried to produce a dry catalyst of fixed Al:Cr ratio, prior to introducing the catalyst to a polymerization reactor. Processes of the invention advantageously eliminate the need for such pre-contacting steps.

[0044] In one embodiment, the invention provides a process of polymerizing ethylene in a slurry reactor, by providing a supported chromium catalyst; providing a cocatalyst selected from metal alkyls of group 13 metals; contacting the catalyst and cocatalyst by cofeeding the catalyst and cocatalyst to the reactor or feeding the catalyst and cocatalyst separately to the reactor, to form a catalyst system; and contacting the catalyst system, under slurry polymerization conditions, with ethylene to form polyethylene. The catalyst and cocatalyst are not contacted prior to the step of feeding or cofeeding, and the process is carried out without addition of alpha-olefin comonomer.

[0045] In another embodiment, the invention provides a process of polymerizing ethylene in a slurry reactor, by providing a supported chromium catalyst activated at a temperature of greater than 600 °C; providing a cocatalyst selected from metal alkyls of group 13 metals; contacting the catalyst and cocatalyst by cofeeding the catalyst and cocatalyst to the reactor or feeding the catalyst and cocatalyst separately to the reactor, to form a catalyst system; and contacting the catalyst system, under slurry polymerization conditions, with ethylene and alpha-olefin comonomer to form polyethylene. The catalyst and cocatalyst are not contacted prior to the step of feeding or cofeeding.

[0046] In another embodiment, the invention provides a process of polymerizing ethylene in a slurry reactor, by providing a supported chromium catalyst; providing a cocatalyst selected from metal alkyls of group 13 metals; contacting the catalyst and cocatalyst by cofeeding the catalyst and cocatalyst to the reactor

or feeding the catalyst and cocatalyst separately to the reactor, to form a catalyst system; and contacting the catalyst system, under slurry polymerization conditions, with ethylene and alpha-olefin comonomer to form polyethylene. The catalyst and cocatalyst are not contacted prior to the step of feeding or cofeeding,  
5 and the polymerization is carried out at a temperature greater than 100 °C.

[0047] In another embodiment, the invention provides a process of polymerizing ethylene in a slurry reactor, by providing a supported chromium catalyst; providing a trialkylaluminum cocatalyst; contacting the catalyst and cocatalyst by cofeeding the catalyst and cocatalyst to the reactor or feeding the catalyst and  
10 cocatalyst separately to the reactor, to form a catalyst system; and contacting the catalyst system, under slurry polymerization conditions, with ethylene and alpha-olefin comonomer to form polyethylene. The catalyst and cocatalyst are not contacted prior to the step of feeding or cofeeding.

[0048] In some embodiments, ethylene is polymerized without intentional  
15 addition of comonomer. Although not wishing to be bound by theory, it is believed that polymerization of ethylene in the presence of a supported chromium catalyst and a cocatalyst generates alpha-olefins as a polymerization by-product. The *in situ* generated alpha-olefin can copolymerize with the ethylene to produce polyethylene copolymer with short chain branching, without addition of  
20 comonomer. The short chain branching decreases polymer density. Increasing the concentration of cocatalyst in the reactor increases the amount of *in situ* comonomer generation, which improves the ESCR and decreases polymer density. It is believed that the *in situ* alpha-olefins produced are short chain alpha-olefins such as butene, hexene, octene and decene, and these comonomers are  
25 believed to provide short chain branches in the copolymer of varying lengths and more evenly distributed in the polymer chain than separately added comonomer. As a result, it is believed that *in-situ* generated comonomer is more effective at improving polymer ESCR than equivalent quantities of added comonomer, for a given polymer density.

30 [0049] In any of the embodiments described herein, hydrogen can be used if desired to control the molecular weight, as is well known in the art.

Product

[0050] The polyethylene produced in the methods of the invention shows improved properties such as environmental stress crack resistance (ESCR). ESCR is a measure of a polyethylene's resistance to cracking under stress and in the presence of an organic reagent such as a surfactant. ESCR is determined in accordance with ASTM D 1693, condition B, 10% IGEPAL™.

[0051] In various embodiments, the polyethylene product has one or more of the following properties:

[0052] an ESCR of at least 50 hr or at least 100 hr or at least 500 hr or at least 750 hr or at least 1000 hr;

[0053] a notched constant tensile load (NCTL) of at least 10 hr or at least 15 hr or at least 25 hr or at least 50 hr;

[0054] a high load melt index ( $I_{21.6}$ ) of from a lower limit of 0.1 or 0.5 or 1 or 10 or 20 or 30 or 40 g/10 min to an upper limit of 100 or 80 or 60, with ranges from any lower limit to any upper limit being contemplated;

[0055] a melt index ( $I_{2.16}$ ) of from a lower limit of 0.01 or 0.1 or 0.5 or 1 or 10 or 20 or 30 or 40 g/10 min to an upper limit of 100 or 80 or 60, with ranges from any lower limit to any upper limit being contemplated; and

[0056] a density of from a lower limit of 0.935 or 0.940 or 0.945 or 0.950 g/cm<sup>3</sup> to an upper limit of 0.960 or 0.955 g/cm<sup>3</sup>, with ranges from any lower limit to any upper limit being contemplated.

[0057] Advantageously, the methods of the present invention can be used to produce polyethylene having consistent ESCR and density.

EXAMPLES

[0058] Environmental Stress Crack Resistance (ESCR) (bent strip) was determined in accordance with ASTM D 1693, condition B, 10% IGEPAL™. IGEPAL™ is a nonylphenoxy poly(ethylenoxy)ethanol surfactant available from Rhone Polenc, Cranbury, NJ. All ESCR values cited herein are ASTM D 1693 condition B, 10% IGEPAL™ F50 values, and are given in units of hours.

[0059] Notched Constant Tensile Load (NCTL) is a stress crack resistance test for highway drainage pipe, and was measured in accordance with ASTM D-5397-99,

using a yield stress of 4000 psi (15% load stress of 600 psi). Each reported value is the average hours to break of five samples.

[0060] Polymer density ( $\text{g/cm}^3$ ) is determined using a compression molded sample, cooled at 15 °C per hour and conditioned for 40 hours at room temperature according to ASTM D1505-68 and ASTM D1928, procedure C.

[0061] Polymer melt flow rates can be determined at 190 °C according to ASTM D-1238-57T.  $I_{21.6}$  is the "flow index" or melt flow rate of the polymer measured according to ASTM D-1238-57T, condition F, and  $I_{2.16}$  is the "melt index" or melt flow rate of the polymer measured according to ASTM D-1238-57T, condition E.

10 The ratio of  $I_{21.6}$  to  $I_{2.16}$  is the "melt flow ratio" or "MFR". The melt flow rate  $I_{21.6}$  is also sometimes termed the "high load melt index" or HLMI. Melt flow rates are reported in units of grams per 10 minutes ( $\text{g}/10 \text{ min}$ ) or equivalently decigrams per minute ( $\text{dg}/\text{min}$ ).

[0062] Several commercially available supported chromium catalysts were used.

15 HA30W and HA30LF are products of W.R. Grace & Co. containing about 1% Cr by weight.

[0063] C-23307, C-25305, C-25307 are titanium-surface modified chromium catalysts available from PQ Corp.

[0064] In the following examples, polymerizations were conducted in a six-liter autoclave equipped with a mechanical overhead stirrer and an external jacket for regulating temperature. In each case, the polymerization was performed by providing continuous addition of ethylene at a fixed total pressure. The reactor had thermocouples to control the temperature of the external jacket and the internal temperature of the reactor during the polymerization. Ethylene fed to the

20 reactor was passed through an electronic gas flow meter to permit continuous monitoring of the ethylene flow to the reactor. All handling of the polymerization reaction components was carried out using airless techniques to exclude oxygen and water. The polymerization was conducted in a slurry of isobutane that had been dried and deoxygenated. All runs were conducted at a reactor temperature

25 between 215 °F and 226 °F (102 to 108 °C) with 180 psi ethylene for a total reactor pressure of 460 to 500 psig (3.2 to 3.5 MPa). Co-polymers of ethylene and 1-hexene were made in some cases, as indicated in the data tables. In each run, the

30



catalyst was first added to the reactor as a dry powder, then cocatalyst added as a solution either in a hydrocarbon solvent, or in the comonomer in the case of copolymerizations, then isobutane diluent added. Upon completion of the polymerization test run (normally 45 to 60 minutes) the reactor was vented to the atmosphere to remove isobutane and unreacted ethylene. The remaining particle form polymer was dried with a nitrogen gas flow at 160 °F (71 °C) for 20 minutes. Finally, the reactor was cooled and the dry polyethylene powder recovered.

[0065] In the data tables, the following abbreviations are used:

[0066] TIBAL = tri-isobutylaluminum

10 [0067] TNOA = tri-n-octylaluminum.

[0068] In Examples 1-56, no comonomer is added. In the remaining examples unless otherwise indicated, hexene was used as comonomer in the indicated amount (cm<sup>3</sup>). In Examples 57-76, the catalyst activation temperature was 815 °C and the reaction temperature was 105 °C.

Table 1

Ex.	Catalyst		Type	Cocatalyst		T <sub>R</sub> ** (°C)	Activity (g/g hr)	Powder			Plaque		
	Type	T <sub>A</sub> * (°C)		mmol	mol ratio Al:Cr			MI (dg/min)	HLMl (dg/min)	Density (g/cm <sup>3</sup> )	HLMl (dg/min)	Density (g/cm <sup>3</sup> )	ESCR (hr)
1	HA30W	480	TIBAL	0.26	4.5	107	2138	0.03	4	0.9498			
2	HA30W	480	TIBAL	0.26	4.5	107	1491	0.03	3.7	0.9450			
3	HA30W	480	TIBAL	0.13	2.25	107	1632	0.02	4.3	0.9558			
4	C25305	480	TIBAL	0.26	4.5	107	1107	0.07	7.7	0.9569	7.5	0.9597	380
5	C25305	480	TIBAL	0.26	4.5	107	2224	0.07	7.5	0.9535	8.3	0.9563	>1000
6	C25305	480	TIBAL	0.13	2.25	107	1965	0.08	8.6	0.9551	10.2	0.9573	565
7	C25305	590	TIBAL	0.26	4.5	105	3372	0.21	15.9	0.9577			
8	C25305	590	TIBAL	0.26	4.5	105	3455	0.25	17.9	0.9480			
9	C25305	590	TIBAL	0.13	2.25	105	1400	0.13	11.9	0.9606			
10	C25305	590	TIBAL	0.26	4.5	103	4458	0.15	11.8	0.9469	7.2	0.9503	562
11	C25305	590	TIBAL	0.26	4.5	103	3686	0.14	14.1	0.9496	8.8	0.9510	>1000
12	C25305	590	TIBAL	0.13	2.25	103	3541	0.17	13.8	0.9539	10.1	0.9555	310
13	C25305	590	TNOA	0.26	4.3	102	4642	0.07	8.1	0.9511	7.4	0.9534	>1000
14	C25305	590	TNOA	0.26	4.3	102	4000	0.1	11.2	0.9497	6.8	0.9523	>1000
15	C25305	590	TNOA	0.26	5.4	107	4542	0.18	11	0.9475	9.7	0.9499	884
16	C25305	590	TNOA	0.26	5.3	107	3926	0.18	13.4	0.9458			
17	C25305	590	TNOA	0.13	2.1	107	4042	0.21	14.6	0.9548	11.1	0.9561	211
18	C25307	480	TIBAL	0.26	4.5	107	2261	0.08	9.0	0.9535	8.3	0.9571	>1000
19	C25307	480	TIBAL	0.26	4.5	107	2202	0.08	8.9	0.9538	9.8	0.9565	768
20	C25307	480	TIBAL	0.13	2.25	107	1892	0.17	17.5	0.9604			
21	C25307	590	TIBAL	0.26	4.5	105	2602	0.19	15.6	0.9491			
22	C25307	590	TIBAL	0.26	4.5	105	2926	0.16	13.2	0.9507	10.6	0.9514	>1000
23	C25307	590	TIBAL	0.13	2.25	105	3163	0.17	13.7	0.9539	10.4	0.9559	593
24	C25307	590	TIBAL	0.26	4.5	103	2309	0.17	13.4	0.9520	8.9	0.9535	>1000
25	C25307	590	TIBAL	0.26	4.5	103	2847	0.11	10.7	0.9542	9.1	0.9468	>1000
26	C25307	590	TNOA	0.13	2.5	107	2437	0.16	16.8	0.9611			
27	C25307	590	TNOA	0.13	2.8	107	2541	0.19	16.1	0.9597			
28	C25307	590	TNOA	0.065	1.5	107	2195	0.17	15.1	0.9614			

\* Catalyst activation temperature

\*\* Reaction temperature

Table 2

Ex.	Catalyst		Cocatalyst			T <sub>R</sub> ** (°C)	Activity (g/g hr)	Powder			Plaque			
	Type	T <sub>A</sub> * (°C)	Type	mmol	mol ratio Al:Cr			MI (dg/min)	HLMI (dg/min)	Density (g/cm <sup>3</sup> )	MI (dg/min)	HLMI (dg/min)	Density (g/cm <sup>3</sup> )	NCTL (hr)
29	C23307	590	TIBAL	0.26	4.5	105	2740	0.15	15.3	0.9508				
30	C23307	590	TIBAL	0.26	4.5	105	2546	0.13	16.2	0.9494				
31	C23307	590	TIBAL	0.13	2.25	105	3361	0.22	18.8	0.9565				
32	C23307	590	TIBAL	0.26	4.5	107	2464	0.27	23.7	0.9502	0.07	13.3	0.9529	91.5
33	C25305	590	TIBAL	0.26	4.5	107	2924	0.12	13.8	0.9494				
34	C25305	590	TIBAL	0.26	4.5	107	3617	0.20	15.0	0.9459				
35	C25305	590	TIBAL	0.13	2.25	107	4456	0.19	16.3	0.9494				
36	C25305	590	TNOA	0.26	4.4	105	2995	0.24	20.2	0.9520	0.09	12.6	0.9537	88.4
37	C25307	590	TIBAL	0.26	4.5	107	2286	0.23	18.8	0.9494	0.11	12.9	0.9521	83.6
38	C25307	590	TIBAL	0.26	4.5	107	2717	0.21	16.5	0.9485				
39	C25307	590	TIBAL	0.13	2.25	107	3187	0.26	19.8	0.9496	0.12	14.5	0.9526	145.3
40	C25307	590	TIBAL	0.26	4.5	107	2624	0.25	21.5	0.9502	0.10	14.6	0.9519	93.3
41	C25307	590	TIBAL	0.13	2.25	107	3046	0.29	22.0	0.9531	0.14	18.3	0.9551	48.5

\* Catalyst activation temperature

\*\* Reaction temperature

Table 3: C25307 Catalyst, with 0.2 cm<sup>3</sup> 1-hexene comonomer

Ex	T <sub>A</sub> <sup>*</sup> (°C)	Cocatalyst		T <sub>R</sub> <sup>**</sup> (°C)	Induction time (min)	Activity (g/g hr)	Powder			Plaque		ESCR (hr)
		Type	mol ratio Al:Cr				MI (dg/min)	HLMl (dg/min)	Density (g/cm <sup>3</sup> )	HLMl (dg/min)	Density (g/cm <sup>3</sup> )	
42	540	TIBAL	1	107	8	1704	0.12	13.67	0.9612	12.4	0.9631	150
43	540	TIBAL	1	107	15	833	0.16	19.26	0.9635	15.8	0.9645	
44	650	TNOA	4	103	2	4280	0.10	8.76	0.9491	5.6	0.9501	> 1000
45	650	TNOA	4	103	1	3660	0.10	8.41	0.9515	5.9	0.9530	592
46	650	TIBAL	4	107	1	3130	0.28	19.09	0.9446	15.1	0.9470	> 1000
47	650	TIBAL	4	107	3	3410	0.25	16.79	0.9446	13.6	0.9475	> 1000
48	540	TNOA	4	107	1	2196	0.07	5.61	0.9557	5.4	0.9566	> 1000
49	540	TNOA	4	107	1	2327	0.04	4.86	0.9555	5.0	0.9567	> 1000
50	650	TIBAL	1	103	12	2120	0.25	17.76	0.9604	13.7	0.9612	90
51	650	TIBAL	1	103	5	2751	0.22	17.55	0.9582	11.1	0.9589	136
52	540	TIBAL	4	103	3	1767	0.04	4.62	0.955	4.7	0.9566	> 1000
53	540	TIBAL	4	103	3	2119	0.03	4.55	0.9565	4.5	0.9573	> 1000
54	650	TNOA	1	107	25	1212	0.32	20.45	0.9599	14.9	0.9620	
55	650	TNOA	1	107	17	2125	0.21	15.79	0.9599	13.1	0.9614	
56	540	TNOA	1	103	17	967	0.11	13.51	0.9629	11.1	0.9640	

\* Catalyst activation temperature

\*\* Reaction temperature

Table 4: HA30LF Catalyst; TIBAL cocatalyst

Ex	mol ratio Al:Cr	Hexene (cm <sup>3</sup> )	Residence Time (min)	Induction Time (min)	Activity (g/g hr)	Powder			Plaque			NCTL (hr)
						MI (dg/min)	HLMl (dg/min)	MI (dg/min)	HLMl (dg/min)	Density (g/cm <sup>3</sup> )		
57	1	0	40	10	2657	0.35	28.5	0.14	17.1	0.9629	6.4	
58	1	1	40	1	3424	0.37	32.9	0.1	15.4	0.9588	9.8	
59	3	0	40	5	4365	0.43	37	0.1	18.3	0.9449	39.8	
60	3	1	40	3	3049	0.71	58.5	0.12	20.3	0.9431	24.5	
61	1	0	60	20	3041	0.2	18.8	0.11	10.9	0.9626	12.1	
62	1	1	60	10	3458	0.21	22.4	0.1	9.2	0.9595	9.1	
63	3	0	60	2	4339	0.35	27.3	0.13	15.8	0.9459	23.1	
64	3	1	60	2	3024	0.28	24.2	0.07	12.2	0.945	54.2	
65	1	0	40	5	2897	0.23	23.1	0.08	12	0.9626	7.5	
66	1	1	40	2	3563	0.24	26.5	0.11	12.1	0.9619	7.5	
67	3	0	40	1	4336	0.42	33.9	0.17	20.4	0.9466	18.2	
68	3	1	40	5	2379	0.73	59.7	0.13	22.8	0.9447	21.9	
69	1	0	60	4	3477	0.22	21.2	0.08	12	0.9618	6.3	
70	1	1	60	3	3079	0.25	26.8	0.07	15.1	0.9600	8.4	
71	3	0	60	2	4532	0.32	22.7	0.05	9.9	0.9475	40.0	
72	3	1	60	4	2543	0.33	32.2	0.11	16.4	0.9489	54.8	
73	2	0.5	50	2	4052	0.38	33.9	0.11	14.4	0.9571	11.3	
74	2	0.5	50	3	4718	0.38	30.2	0.08	13	0.9492	15.7	
75	2	0.5	50	2	4171	0.33	28.3	0.09	13.8	0.9494	20.3	
76	2	0.5	50	4	4325	0.37	31.7	0.08	15.6	0.9479	36.4	

[0069] All patents, test procedures, and other documents cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent with this invention and for all jurisdictions in which  
5 such incorporation is permitted.

[0070] Having thus described the invention in detail, the following sets forth, without limitation, particular preferred embodiments:

[0071] a method of forming a catalyst system in a polymerization reactor, the method characterized by: (a) providing a supported chromium catalyst; (b)  
10 providing a trialkylaluminum cocatalyst of formula  $AlR_3$ , where each R group is independently a linear or branched  $C_4$ - $C_{12}$  alkyl group; and (c) contacting the catalyst and cocatalyst by: (i) cofeeding the catalyst and cocatalyst to the reactor, wherein the catalyst and cocatalyst are not contacted prior to the step of cofeeding, or (ii) feeding the catalyst and cocatalyst separately to the reactor, wherein the  
15 catalyst and cocatalyst are not contacted prior to the step of feeding, to form a catalyst system;

[0072] including one or more of the following more preferred embodiments: wherein the supported chromium catalyst comprises chromium supported on a silica-titania support; wherein the supported chromium catalyst comprises  
20 titanium surface-modified supported chromium catalyst; wherein each R is independently a linear or branched  $C_4$  to  $C_8$  alkyl group; wherein the cocatalyst comprises tri-isobutylaluminum or tri-n-octylaluminum; wherein the polymerization reactor is a slurry reactor; wherein the supported chromium catalyst is activated by heating to a temperature of from 400 °C to 900 °C; or even  
25 more preferably wherein the supported chromium catalyst is activated by heating to a temperature of from greater than 600 °C to 900 °C;

[0073] and also a catalyst system formed by the foregoing;

[0074] and a process of polymerizing ethylene characterized by contacting, under polymerization conditions, ethylene and the catalyst system according to the present invention;

[0075] and a process of polymerizing ethylene characterized by contacting, under  
5 polymerization conditions, ethylene, alpha-olefin comonomer, and the catalyst system according to the present invention;

[0076] and a polyethylene resin formed by the processes of polymerizing ethylene using the catalyst according to the foregoing;

[0077] and an article comprising the polyethylene resin made by a process  
10 according to the present invention, especially as characterized by the foregoing preferred and more preferred embodiments.

[0078] Another particularly preferred embodiment is a process of polymerizing ethylene in a polymerization reactor, the process characterized by: (a) providing a supported chromium catalyst; (b) providing a cocatalyst selected from metal  
15 alkyls of group 13 metals; (c) contacting the catalyst and cocatalyst by: (i) cofeeding the catalyst and cocatalyst to the reactor, wherein the catalyst and cocatalyst are not contacted prior to the step of cofeeding, or (ii) feeding the catalyst and cocatalyst separately to the reactor, wherein the catalyst and cocatalyst are not contacted prior to the step of feeding, to form a catalyst system;  
20 and (d) contacting the catalyst system, under polymerization conditions, with ethylene, wherein the process is carried out without addition of alpha-olefin comonomer;

[0079] and including one or more of the following more preferred embodiments:

[0080] wherein the supported chromium catalyst comprises chromium supported  
25 on a silica-titania support; wherein the supported chromium catalyst comprises titanium surface-modified supported chromium catalyst; wherein the cocatalyst comprises a compound of formula  $MR_3$ , where M is a Group 13 metal, and each R is independently a linear or branched  $C_1$  to  $C_{12}$  alkyl group; wherein each R is independently a linear or branched  $C_2$  to  $C_{10}$  alkyl group; wherein each R is  
30 independently a linear or branched  $C_4$  to  $C_8$  alkyl group; wherein M is boron; wherein each R is ethyl; wherein M is aluminum; wherein each R is independently a  $C_4$  to  $C_{12}$  alkyl group; wherein the cocatalyst comprises tri-isobutylaluminum or

tri-n-octylaluminum; wherein the polymerization is carried out at a temperature of from 80 °C to 120 °C; wherein the polymerization is carried out at a temperature greater than 100 °C; wherein the polymerization is carried out at a temperature of from greater than 100 °C to 110 °C; wherein the catalyst is activated by heating to a temperature of from 400 °C to 900 °C or even more preferably wherein the catalyst is activated by heating to a temperature of from greater than 600 °C to 900 °C; wherein the polymerization reactor is a slurry reactor;

[0081] and also a polyethylene resin formed by and of the foregoing processes;

[0082] and also an article comprising the polyethylene resin made by a process according to the foregoing preferred and more preferred embodiments.

[0083] Yet another particularly preferred embodiment is:

[0084] a process of polymerizing ethylene in a polymerization reactor, the process characterized by: (a) providing a supported chromium catalyst activated at a temperature of greater than 600 °C; (b) providing a cocatalyst selected from metal alkyls of group 13 metals; (c) contacting the catalyst and cocatalyst by: (i) cofeeding the catalyst and cocatalyst to the reactor, wherein the catalyst and cocatalyst are not contacted prior to the step of cofeeding, or (ii) feeding the catalyst and cocatalyst separately to the reactor, wherein the catalyst and cocatalyst are not contacted prior to the step of feeding, to form a catalyst system; and (d) contacting the catalyst system, under polymerization conditions, with monomers comprising ethylene and alpha-olefin comonomer;

[0085] and a particularly preferred embodiment of polymerizing ethylene in a polymerization reactor, the process comprising: (a) providing a supported chromium catalyst; (b) providing a cocatalyst selected from metal alkyls of group 13 metals; (c) contacting the catalyst and cocatalyst by: (i) cofeeding the catalyst and cocatalyst to the reactor, wherein the catalyst and cocatalyst are not contacted prior to the step of cofeeding, or (ii) feeding the catalyst and cocatalyst separately to the reactor, wherein the catalyst and cocatalyst are not contacted prior to the step of feeding, to form a catalyst system; and (d) contacting the catalyst system, under polymerization conditions, with monomers comprising ethylene and alpha-olefin comonomer, wherein the polymerization is carried out at a temperature greater than 100 °C;



[0086] and wherein either of the two immediately foregoing particularly preferred embodiments including one or more of the following more preferred embodiments: wherein the supported chromium catalyst comprises chromium supported on a silica-titania support; wherein the supported chromium catalyst  
5 comprises titanium surface-modified supported chromium catalyst; wherein the cocatalyst comprises a compound of formula  $MR_3$ , where M is a Group 13 metal, and each R is independently a linear or branched  $C_1$  to  $C_{12}$  alkyl group; wherein each R is independently a linear or branched  $C_4$  to  $C_8$  alkyl group; wherein M is boron; wherein each R is ethyl; wherein M is aluminum; wherein each R is  
10 independently a  $C_4$  to  $C_{12}$  alkyl group; wherein the cocatalyst comprises tri-isobutylaluminum or tri-n-octylaluminum; wherein the polymerization is carried out at a temperature of from 80 °C to 120 °C; wherein the polymerization is carried out at a temperature greater than 100 °C; wherein the polymerization is carried out at a temperature of from greater than 100 °C to 110 °C; wherein the  
15 catalyst is activated by heating to a temperature of from 400 °C to 900 °C; wherein the catalyst is activated by heating to a temperature greater than 600 °C; wherein the polymerization reactor is a slurry reactor;

[0087] and also the polyethylene resin formed by the foregoing;

[0088] and also an article comprising the polyethylene resin made by the  
20 foregoing processes.

[0089] Moreover, another particularly preferred embodiment of the present invention is a process of polymerizing ethylene in a polymerization reactor, the process characterized by: (a) providing a supported chromium catalyst; (b) providing a trialkylaluminum cocatalyst of formula  $AlR_3$ , where each R group is  
25 independently a linear or branched  $C_4$ - $C_{12}$  alkyl group; (c) contacting the catalyst and cocatalyst by: (i) cofeeding the catalyst and cocatalyst to the reactor, wherein the catalyst and cocatalyst are not contacted prior to the step of cofeeding, or (ii) feeding the catalyst and cocatalyst separately to the reactor, wherein the catalyst and cocatalyst are not contacted prior to the step of feeding, to form a  
30 catalyst system; and (d) contacting the catalyst system, under slurry polymerization conditions, with monomers comprising ethylene and alpha-olefin comonomer;

[0090] including one or more of the following preferred embodiments: wherein the supported chromium catalyst comprises chromium supported on a silica-titania support; wherein the supported chromium catalyst comprises titanium surface-modified supported chromium catalyst; wherein each R is independently a linear  
5 or branched C<sub>4</sub> to C<sub>8</sub> alkyl group; wherein the cocatalyst comprises tri-isobutylaluminum or tri-n-octylaluminum; wherein the polymerization is carried out at a temperature of from 80 °C to 120 °C; wherein the polymerization is carried out at a temperature greater than 100 °C; wherein the polymerization is carried out at a temperature of from greater than 100 °C to 110 °C; wherein the  
10 catalyst is activated by heating to a temperature of from 400 °C to 900 °C; wherein the catalyst is activated by heating to a temperature greater than 600 °C; wherein the polymerization reactor is a slurry reactor;

[0091] and also a polyethylene resin formed by the foregoing;

[0092] and an article comprising the polyethylene resin formed by the foregoing.

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[0093] What is claimed is:

CLAIMS

1. A method of forming a catalyst system in a polymerization reactor, the method characterized by:
  - (a) providing a supported chromium catalyst;
  - 5 (b) providing a trialkylaluminum cocatalyst of formula  $AlR_3$ , where each R group is independently a linear or branched  $C_4$ - $C_{12}$  alkyl group; and
  - (c) contacting the catalyst and cocatalyst by:
    - 10 (i) cofeeding the catalyst and cocatalyst to the reactor, wherein the catalyst and cocatalyst are not contacted prior to the step of cofeeding, or
    - (ii) feeding the catalyst and cocatalyst separately to the reactor, wherein the catalyst and cocatalyst are not contacted prior to the step of feeding,
- 15 to form a catalyst system.
2. The method of claim 1, wherein the supported chromium catalyst comprises chromium supported on a silica-titania support.
- 20 3. The method of claim 1, wherein the supported chromium catalyst comprises titanium surface-modified supported chromium catalyst.
4. The method of any of the preceding claims, wherein each R is independently a linear or branched  $C_4$  to  $C_8$  alkyl group.
- 25 5. The method of any of the preceding claims, wherein the cocatalyst comprises tri-isobutylaluminum or tri-n-octylaluminum.
6. The method of any of the preceding claims, wherein the polymerization  
30 reactor is a slurry reactor.

7. The method of any of the preceding claims, wherein the supported chromium catalyst is activated by heating to a temperature of from 400 °C to 900 °C, preferably by heating to a temperature of from greater than 600 °C to 900 °C.
- 5 8. A catalyst system formed by the method of any of the preceding claims.
9. A process of polymerizing ethylene comprising contacting, under polymerization conditions, ethylene and the catalyst system of claim 8.
- 10 10. A process of polymerizing ethylene comprising contacting, under polymerization conditions, ethylene, alpha-olefin comonomer, and the catalyst system of claim 8.
- 15 11. A process of polymerizing ethylene comprising contacting, under polymerization conditions, ethylene and the catalyst system of claim 8, without addition of alpha-olefin.
12. A polyethylene resin formed by the process of claim 10 or 11.
- 20 13. An article comprising the polyethylene resin of claim 12.

## INTERNATIONAL SEARCH REPORT

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0279890	A	31-08-1988	US 4735931 A	05-04-1988
			CA 1292734 C	03-12-1991
			DE 3777629 D1	23-04-1992
			EP 0279890 A2	31-08-1988
			ES 2030018 T3	16-10-1992
			HU 48646 A2	28-06-1989
			JP 2071044 C	10-07-1996
			JP 7103178 B	08-11-1995
			JP 62297305 A	24-12-1987
			NO 872486 A ,B,	17-12-1987
			SG 78192 G	04-12-1992
			US 4820785 A	11-04-1989
WO 0132307	A	10-05-2001	AU 3792201 A	14-05-2001
			CA 2389654 A1	10-05-2001
			CN 1391498 T	15-01-2003
			EP 1235645 A1	04-09-2002
			HU 0203283 A2	28-01-2003
			NO 20022099 A	24-06-2002
			WO 0132307 A1	10-05-2001
DE 2622755	A	08-12-1977	DE 2622755 A1	08-12-1977
			FR 2352002 A1	16-12-1977
US 4877763	A	31-10-1989	US 4818800 A	04-04-1989
EP 1172381	A	16-01-2002	EP 1172381 A1	16-01-2002
			JP 2002080521 A	19-03-2002
			US 2002042482 A1	11-04-2002
US 5096868	A	17-03-1992	AU 2348288 A	27-04-1989
			CA 1323361 C	19-10-1993
			EP 0314385 A2	03-05-1989
			JP 1213312 A	28-08-1989
US 6174981	B1	16-01-2001	NONE	